

The crosslinker exemplified herein is a polyfunctional aziridine liquid crosslinker, such as, for example, 1-aziridinepropanoic acid, 2-methyl-, 2 ethyl-2-(3-(2-methyl-1-

~~WHAT IS CLAIMED IS:~~ methyl)-1,3-propanediyl ester marketed by Zeneca Resin,

Wilmington, Delaware. A graft coated substrate, the substrate comprising polyethylene, and a graft coating covalently bonded thereto, wherein said graft coating comprises a non-polyethylene polymer or copolymer reactive carboxyl functionality, in both water-based and organic solvent.

2. The graft coated substrate of claim 1, wherein the graft coating comprises a polymer selected from the group consisting of a urethane, an epoxy, a polysilicone, and by combinations or copolymers thereof and the like. For those embodiments comprising epoxy

monomers. 3. The graft coated substrate of claim 1 wherein the graft coating comprises agents materials selected from the group consisting of a pigment or colorant, a fire retarding agent, and combinations thereof; curing agents or hardeners, e.g., including those comprising

trimethylolpropane triisocyanate from Air Products. 4. The graft coated substrate of claim 1 wherein the substrate comprises a polyethylene having a density ranging from about 0.930 g cm⁻³ to about 0.940 g cm⁻³.

5. The graft coated substrate of claim 1 that comprises a polyethylene having an average molecular weight ranging from about 100,000 amu to at least 6 x 10⁶ amu.

The Grafting Solution and Process
Parts A and B are mixed in a suitable proportion, stirred to a uniform solution, and the 6. The graft coated substrate of claim 1, wherein the substrate comprises a resulting grafting solution is applied to the PE substrate to be treated. The time necessary for polyethylene selected from the group consisting of low density polyethylene, a linear low density polyethylene, a medium density polyethylene, a high density polyethylene, a high and the desired properties of the grafted PE. Generally, the solution is air dried onto the PE substrate, and then cured by the application of heat for a time period ranging, e.g., from about polyethylene, an ultra-high density polyethylene, and combinations thereof.

1 to about 4 hours, at a temperature ranging, e.g., from about 100 to about 150 degrees F. 7. The graft coated substrate of claim 1 that is formed into an article of manufacture. When heat curing is undesirable, the coated substrate can optionally be allowed to cure at selected from the group consisting of a pipe or tube, a curved or planar sheet, a beam, a ambient temperature, e.g., 25-30 degrees C. for up to 5 or more days; board, a rod or shaft, a container for solids or fluids, and combinations thereof.

8. The graft coated substrate of claim 7 wherein the pipe is selected from the group consisting of straight pipe, bent pipe, a straight pipe joint, an elbow joint, an end-cap, a heat-shrinkable joint, and combinations thereof. Confirming the Properties of the Grafted Surface

The graft coatings were also tested for their ability to resist melting and catching fire for a time period, by exposure to a standardized source of intense radiant heat, as described in 9. The graft coated substrate of claim 7 wherein the pipe is selected from the group consisting of single wall pipe, pipe with a plurality of walls nested one within the other, pipe with a single insulating layer between two concentric walls, and pipe with a plurality of

concentric insulating layers.
Surface Energy Testing

10. The graft coated substrate of claim 1 that resists melting and burning for a time period ranging from about 1 to about 18 minutes, when the article is tested by exposure to a adhesion of paints, cements, adhesives and the like to surfaces. The graft coated surfaces of planar heated surface that is heated to a temperature ranging from about 800 to about 960°C,

and wherein the heating panel is a rectangle that measures about 25 x 51 cm, and the graft coated substrate is positioned at a distance of about 12.5 cm from the heating panel.

11. The graft coated substrate of claim 1 that has a surface energy ranging from about 56 to about 80 dynes/cm².

12. The graft coated substrate of claim 1 that has a surface energy of at least 80 dynes/cm².

13. A process for modifying the surface of a solid polyethylene substrate, comprising covalently grafting a heat resistant coating onto said substrate by

- (a) applying to a solid polyethylene substrate, a liquid composition comprising effective amounts of a monomer, prepolymer, a graft initiator, a catalyst and a polymerization promoter, under conditions effective to promote grafting of the monomer or prepolymer to the solid polyethylene substrate to form a coating on the substrate, and
- (b) curing the applied composition.

14. The process of claim 13 wherein the monomer or prepolymer is selected from the group consisting of a vinyl monomer, a urethane monomer, an epoxy monomer, a silicon-based monomer and combinations thereof.

15. The process of claim 13 wherein the graft initiator is a metal ion, present in an amount effective to initiate radical formation in the polyethylene substrate.

16. The process of claim 15 wherein the graft initiator is present in a concentration ranging from about 0.01 to about 1.0%, by weight.

17. The process of claim 15 wherein the graft initiator is selected from the group consisting of ions of iron, silver, cobalt, copper, cerium and combinations thereof.

18. The process of claim 13 wherein the catalyst is a peroxide present in the liquid composition in a concentration ranging from about 0.1 to about 5% by weight.

19. The process of claim 13 wherein the catalyst is selected from the group consisting of benzoyl peroxide, methyl ethyl ketone peroxide, 1-butyl hydroperoxide and combinations thereof.

20. The process of claim 13 wherein the polymerization promoter is present in a concentration effective to react with, and crosslink, the monomer or prepolymer.

21. The process of claim 20 wherein the polymerization promoter is a polyfunctional aziridine liquid crosslinker.

22. The process of claim 13 wherein the substrate is a polyethylene having a density ranging from about 0.930 g cm⁻³ to about 0.940 g cm⁻³.

PART B

Crosslinker CX-100

1.8

28

9011-1001

Preparation of Part A
 The process of claim 13 wherein the liquid composition is applied to the substrate by a method selected from the group consisting of brushing, dipping, spraying and combinations thereof.

5 The composition was added in the weight proportions shown by Table 1, *supra*.
 24 The process of claim 13 wherein the applied composition is self-curing.

5 The result was then stirred to form a uniform solution of Part A.
 25 The process of claim 13 wherein the applied composition is cured by heating the coated substrate at a temperature and for a duration sufficient to cure the applied coating.

26. The process of claim 25 wherein the applied composition is cured at a temperature ranging from about 60 to about 200 degrees F, for a time period ranging from about 30 minutes to about 6 days.
 Preparation of the FORMULATION:
 The Part A solution was mixed into a separate container with the Part B solution, in the weight proportions shown above by Table 1. The mixed formulation was stirred to a

10 27. The process of claim 13 wherein the liquid composition further comprises a uniform solution for the grafting process.
 10 compatible flame retardant agent.

28. The process of claim 27 wherein the flame retardant agent is a phosphorous-based flame retardant.
 Application of the Grafting Coating:
 15 The polyethylene samples and related parts were coated with the grafting solution by spraying.

15 29. The process of claim 27 wherein the flame retardant agent is selected from the group consisting of chlorinated phosphate esters, melamine derivatives, oligomeric phosphate esters, bromoaryl ether/phosphate product, and phosphonates.
 150 For at ambient conditions (25°C, 50% RH) for various characteristics.

30. The process of claim 27 wherein the flame retardant is selected from the group consisting of dimethyl methylphosphonate, diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate, oligomeric chloroalkyl phosphate/phosphonate, tri (1, 3-dichloroisopropyl) phosphate, oligomeric phosphonate, tributyl phosphate, isopropylated triphenyl phosphate ester, and combinations thereof.
 EXAMPLE 2
 Water-Based Grafting Formulation with Urethane Prepolymer

31. The process of claim 30 wherein the flame retardant agent is dimethyl methylphosphonate.
 25 In addition to the water-based grafting formulation of Example 1, water-based formulations were also prepared. Table 2, below, provides a water-based urethane formula.

32. The process of claim 13 wherein the liquid composition is first prepared without the polymerization promoter, and the process further comprises the step of mixing the polymerization promoter with the liquid composition prior to application of the liquid composition to the substrate.
 Table 2
 Parts by Weight

33. The process of claim 13 wherein the liquid composition further comprises a polymer selected from the group consisting of a vinyl polymer, a urethane, an epoxy, a polysilicone and combinations thereof, wherein said polymer is suitable for grafting to the substrate.
 30 (Witco OrganoSilicones Group/OSi Specialties, Inc.)

34. A solid polyethylene substrate comprising a graft coating covalently bonded thereto, prepared by the process of claim 13.

36. A liquid composition for graft coating a solid polyethylene substrate with a graft that comprises at least one non-polyethylene polymer, comprising an effective amount of a monomer or prepolymer, a graft initiator, a catalyst and a polymerization

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Orbitron propylene (Reedley 9679) was taken to be a promoter and is if were added.

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